

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 6 :</b> <b>C11D 3/00, 3/37, 3/386</b>		<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/06098</b>
			<b>(43) International Publication Date:</b> 2 March 1995 (02.03.95)
<b>(21) International Application Number:</b> PCT/GB94/01882			<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).
<b>(22) International Filing Date:</b> 30 August 1994 (30.08.94)			
<b>(30) Priority Data:</b> 9317803.6 27 August 1993 (27.08.93) GB			
<b>(71) Applicant (for all designated States except US):</b> CUSSENS (INTERNATIONAL) LIMITED [GB/GB]; Bridgewater House, 60 Whitworth Street, Manchester M1 6LU (GB).			
<b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> HALLIWELL, Duncan, Cooper [GB/GB]; 45 Higher Ridings, Bromley Cross, Bolton BL7 9HD (GB). ASPIN, Paul [GB/GB]; 2 Hood Close, Tyldesley M29 8PN (GB). HARRISON, Andrew, John [GB/GB]; 3 Coney Walk, Saughall Massey, Upton, Wirral, Merseyside L69 3RB (GB).			
<b>(74) Agent:</b> ATKINSON, Peter, Birch; Marks & Clerk, Suite 301, Sunlight House, Quay Street, Manchester M3 3JY (GB).			<b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> LAUNDRY DETERGENT COMPOSITION			
<b>(57) Abstract</b> <p>A laundry detergent composition comprises at least one surface active agent and a polyvinylpyrrolidone having a molecular weight greater than 1,000,000. The high molecular weight PVP is particularly effective for scavenging dye during washing and preventing its redeposition on other garments in the same wash load. An optional further component is a cellulase.</p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

LAUNDRY DETERGENT COMPOSITION

The present invention relates to a laundry detergent composition intended particularly but not exclusively for domestic laundering operations.

One problem which may be encountered in laundry operations is that dye from one garment may become dissolved in the wash water and then deposit on one or more other garments causing discolourations thereof. The problem can be particularly acute if garments of a relatively dark or deep colour are washed together with light coloured (e.g. white) or mixed garments which can become significantly discoloured.

It is known that polyvinylpyrrolidone (PVP), when incorporated in a laundry detergent formulation, will act as a dye transfer inhibitor.

Thus, for example, WO-A-9218598 proposes a composition having colour care properties and containing a polyvinylpyrrolidone polymer having a molecular weight of 5,000 to 1,000,000, more preferably from 5,000 to 50,000, most preferably from 8,000 to 15,000. In addition to a surface active agent, the composition also contains an alkaline cellulase. Furthermore, WO-A-9218597 discloses a laundry detergent composition containing polyvinylpyrrolidone having a molecular weight of 5,000 to 22,000. This formulation may also contain a cellulase.

We have now surprisingly found that the use, in a laundry detergent composition, of polyvinylpyrrolidone having a higher molecular weight than previously proposed for use in laundering operations leads to improved colour care performance.

Therefore according to the present invention there is provided a laundry detergent composition comprising at least one surface active agent and a polyvinylpyrrolidone having a molecular weight of greater than 1,000,000.

Molecular weight of polyvinylpyrrolidone as used in the invention is determined by SEC/LALLS (Size Exclusion Chromatography/Low Angle Laser Light Scattering) using the method disclosed in Journal of Liquid. Chromatography, 10(6), 1127-1150(1987) (Senak et al).

We have found that PVP having a weight average molecular weight greater than 1,000,000 is particularly effective for scavenging

dye during washing and preventing its re-deposition on other garments in the same wash load.

Preferably the polyvinylpyrrolidone has a molecular weight of at least 1,200,000, more preferably at least 1,500,000. The molecular weight of the PVP may, for example, be 1,500,000 to 4,000,000. More preferably the molecular weight of the PVP may be in the range 2,000,000 to 4,000,000, e.g. 2,400,000 to 3,400,000. A particularly preferred molecular weight is about 2,900,000.

Examples of PVP which may be used include K-120 (molecular weight 2,540,000 to 3,220,000) and K-90 (molecular weight 1,270,000 to 1,710,000), both obtainable from ISP Europe.

Typically the PVP will be present in the formulation in an amount of 0.01 to 2.0% by weight (e.g. 0.05 to 2.0% by weight).

In addition to the PVP, the other essential ingredient of the formulation of the invention is a surface active agent. The surfactant used is preferably an anionic and/or non-ionic surfactant. It is however also possible to use zwitterionic or amphoteric surface active agents.

Preferred anionic surfactants are anionic surfactant acids. Examples include alkyl aryl sulphonic acids, fatty acid sulphonic acids, olefin sulphonic acids, fatty alcohol ether sulphuric acid, fatty methyl ester sulphonic acid, and alkane sulphonic acids. It is particularly preferred that the surfactant acid is an alkyl aryl sulphonic or sulphuric acid containing an alkyl group with 9-20 carbon atoms and a sulphonic or sulphuric acid ester group (included in the term alkyl is the alkyl portion of the aryl groups), or a fatty acid sulphuric acid obtained by sulphating alcohols with an 8-18 carbon atom chain. Especially useful are linear straight chain alkyl benzene sulphonic acids in which the average number of carbon atoms in the alkyl group is 11 to 13.

The amount of anionic surfactant is preferably in the range 1% to 40% (e.g. 5% to 40%) with values toward the lower end of this range being preferred. Thus the preferred amount of anionic surfactant is 1% to 30% by weight, more especially 5% to 25% by weight (e.g. 7 to 25% by weight).

It is preferred that a non-ionic surfactant is included in the formulation due to their good detergency properties. Preferred non-

ionics are water-soluble alcohol ethoxylates of HLB lower than 13. Such non-ionics are preferably C<sub>12</sub>-C<sub>18</sub> linear primary alcohols with 3 to 30 moles of ethylene oxide per mole of alcohol.

The amount of non-ionic surfactant present is preferably 1% to 15% (e.g. 1% to 10%) by weight.

Mixtures of surfactants may be used.

It is highly preferred that the detergent composition also incorporates a cellulase. The function of the cellulase (in relation to garments containing cellulosic, e.g. cotton fibres, is to digest microfibrils which are generated on the fibres. This prevents pilling of the garment and reduces reflectance. We have found that there is synergy between the higher molecular weight PVP used in the invention (i.e. molecular weight greater than 1,000,000) and cellulase in reducing reflectance of the fabric caused by fibrils generated by normal wear of the garment.

Examples of cellulases which may be used are those exemplified in WO-A-9218598. Generally the amount of cellulase used will be in the range 0.05% to 4% (e.g. 1% to 4%) by weight of the composition.

The formulation will generally also include a builder usually in an amount of 15% to 50% by weight. The preferred builders are phosphates, particularly sodium tripolyphosphate and ortho- and pyrophosphates. An alkaline material may also be included, e.g. in an amount 15% to 35%, to provide performance benefits in the laundering process. The preferred alkaline material is sodium carbonate.

Other components which may be present in the formulation, the typical amounts in which they may be present, and specific examples thereof are shown in the following table.

<u>Component</u>	<u>Amount</u>	<u>Example</u>
Filler	0-50%	Sodium Sulphate
Anti-Redeposition Agent	0.5-5%	Sodium Carboxymethyl Cellulose
Corrosion Inhibitor	0-5%	Sodium Metasilicate
Sequestering Agent	0%-5% EDTA	
Perfume	<1%	
Optical Brightener	<1%	

It is preferred that the detergent formulation in accordance with the invention is in powder or granular form. A particularly suitable method of producing such a powder or granular formulation is as disclosed in EP-A-0 353 976 (Cussons)

To produce formulations in accordance with the invention using this procedure, particulate solids to be incorporated in the composition are blended in a fluidisation process and then the liquids are sprayed onto the blend. This results in agglomeration of particles to form granules of various particle sizes ranging from 2 mm to less than 75 microns.

Typically formulations in accordance with the invention will be used in amounts sufficient to give up to 100 mg of PVP per litre of wash liquor, more preferably less than 40 mg l<sup>-1</sup>.

One specific formulation in accordance with the invention is as follows.

Sodium Tripolyphosphate	40.000%
Light Sodium Carbonate	25.000%
Sodium Sulphate	8.500%
Polyvinyl Pyrrolidone (K-120 ex ISP Europe)	0.500%
Anti-Redeposition Agent	2.500%
Nonionic (Alcohol Ethoxylate)	4.000%
OBA	0.075%
Sequestering Agent	0.500%
Alkyl Benzene Sulphonic Acid	14.000%
Cellulase	0.500%
Perfume and Other Incidental Ingredients	4.425%

The invention is illustrated by the following non-limiting Examples.

#### Example 1

Three detergent compositions were tested to evaluate their effectiveness in retarding dye staining of cotton fabrics. The compositions are detailed below.

Composition A (Invention)

Sodium Tripolyphosphate	31% by weight
Sodium Carbonate	27% by weight
Sodium Sulphate	12.5%
Sodium Bicarbonate	13%
Sodium Carboxymethylcellulose	4%
Alkyl Benzene Sulphonic Acid	8%
Polyvinylpyrrolidone (K-120 ex ISP)	0.5%
Celluzyme 0.7T (ex Novo)	0.35%
Perfume, Antifoam, EDTA	1.65%
Ethoxylated Nonionic Surfactant	2%

Composition B (Comparative)

As for composition A but replacing PVP K-120 by PVP HP50 available from BASF. According to the manufactures literature, HP50 has a molecular weight of 40,000.

Composition C (Comparative)

A commercially available detergent containing neither PVP nor a cellulase enzyme.

Procedure

The above formulations were tested to determine their effectiveness in preventing deposition of dye (Solophenyl Blue GL) on white cotton fabric (scoured and bleached). The procedure was effected by washing the fabric in the presence of the dye in accordance with the conditions set out below using a Jefferies Rotadyer. This procedure was used because a known amount of dye is used and the results are more reproducible than is the case of a dyed fabric which can release dye on washing and cross-stain other fabrics.

Amounts Used:	Composition A	7g/litre
	Composition B	7g/litre
	Composition C	10g/litre

Fabric to liquor ratio 1:10

Test fabric: - 100% white cotton, scoured and bleach

Water hardness - Tap water (30 ppm  $\text{CaCO}_3$ )

Wash duration - 1 hour in Jefferies Rotadyer plus rinsing and drying (via tumble dryer)

Wash temperature - 40 and 60°C

Dye to PVP ratio 1:1 and 0.5:1

### Results

Results were measured on an ICS/Texacon Micromatch MM2000 reflectometer using Cielab L and b values (i.e. lightness and blueness). The results are shown in Table 1.

TABLE 1

<u>Detergent</u>	<u>Wash Temp</u>	<u>Dye/PVP Ratio</u>	<u>L Value</u>	<u>b Value</u>
A	40°C	1:1	91.160	+0.096
B	40°C	1:1	90.354	-1.118
C	40°C	1:1	80.980	-11.716
A	40°C	0.5:1	92.352	+1.368
B	40°C	0.5:1	92.201	+1.119
C	40°C	0.5:1	85.964	-6.719
A	60°C	1:1	87.934	-4.148
B	60°C	1:1	86.390	-5.558
C	60°C	1:1	77.976	-14.413
A	60°C	0.5:1	91.051	-0.412
B	60°C	0.5:1	89.635	-1.046
C	60°C	0.5:1	83.150	-9.326

### Notes

L Values:- The higher the L value, the whiter the fabric

b Values: - The more negative the b values, the bluer the fabric

The results clearly show that compositions in accordance with the invention give rise to higher L values and lower b values than



either of the comparative compositions. Therefore these results show that compositions in accordance with the invention, incorporating the higher molecular weight PVP, are more effective for preventing dye deposition than the comparative compositions, including those which incorporate a lower molecular weight PVP.

### Example 2

Six detergent formulations were tested to determine the effectiveness of PVP having a molecular weight greater than 1,000,000 and cellulase in reducing reflectance of fabrics. The detergent formulations were as follows:

	<u>Formulation No.</u>					
	1	2	3	4	5	6
Sodium Bicarbonate	30%	30%	30%	30%	30%	30%
Sodium	30%	30%	30%	30%	30%	30%
Tripolyphosphate						
Dodecyl Benzene	10%	10%	10%	10%	10%	10%
Sulphonic Acid						
Sodium Sulphate	30%	28.57%	29.3%	29.3%	27.87%	27.87%
Celluzyme 0.7T	-	1.43%	-	-	1.43%	1.43%
PVP HP50	-	-	0.7%	-	0.7%	-
PVP K-120	-	-	-	0.7%	-	0.7%

The tests were carried out on a black cotton fabric which had previously been washed in a detergent formulation containing neither PVP nor cellulase enzyme.

The L value for each fabric was determined (after the aforementioned 2 washes) using an ICS/Texacon Micromatch MM2000 reflectometer.

The fabrics were then washed 10 times using formulations 1-6. The washing was carried out in a Tergotometer at 40°C for 30 minutes using an agitator speed of 90 rpm. The amount of each detergent formulation used was 10 g l<sup>-1</sup> and the water had a hardness of 30 ppm CaCO<sub>3</sub>.

After washing, the L value of each fabric was again determined. For each fabric the value of  $\Delta L$  was determined using the following

formula

$$\Delta L = L_2 - L_1$$

where  $L_2$  = L value of fabric after the 10 washes

$L_1$  = L value of fabric prior to the 10 washes.

The results are shown in the Table 2.

Table 2

<u>Formulation No.</u>	<u>L</u>
1	+0.916
2	+0.236
3	+0.116
4	+0.246
5	+0.276
6	-0.659

A positive value of  $\Delta L$  indicates that the black fabric is becoming lighter, i.e. the large positive value of  $\Delta L$  the greyer the fabric is becoming. Conversely a negative value of  $\Delta L$  indicates that the fabric is becoming darker. With the exception of formulation 6, the values of  $\Delta L$  are positive showing that detergent formulations 1-5 result in increasing greyness of the fabric. It was only for formulation 6 that a negative value of  $\Delta L$  was obtained, showing that reflectance had been reduced.

These results clearly demonstrate the synergistic effect obtained by using a combination of PVP K-120 and Celluzyme 0.7T.

CLAIMS

1. A laundry detergent composition comprising at least one surface active agent and a polyvinylpyrrolidone having a molecular weight of greater than 1,000,000.
2. A composition as claimed in claim 1 wherein the polyvinylpyrrolidone has a molecular weight of at least 1,200,000.
3. A composition as claimed in claim 2 wherein the polyvinylpyrrolidone has a molecular weight of at least 1,500,000.
4. A composition as claimed in claim 3 wherein the molecular weight of the polyvinylpyrrolidone is 1,500,000 to 4,000,000.
5. A composition as claimed in claim 4 wherein the polyvinylpyrrolidone has a molecular weight in the range 2,400,000 to 3,400,000.
6. A composition as claimed in any one of claims 1 to 5 wherein the polyvinylpyrrolidone is present in the formulation in an amount of 0.01% to 2.0% by weight.
7. A composition as claimed in any one of claims 1 to 6 wherein the surfactant comprises an anionic surfactant.
8. A composition as claimed in claim 7 wherein the anionic surfactant is an alkyl aryl sulphonic acid.
9. A composition as claimed in claim 8 wherein the anionic surfactant is a linear straight chain alkyl benzene sulphonic acid in which the average number of carbon atoms in the alkyl group is 11 to 13.
10. A composition as claimed in any one of claims 7 to 9 wherein the anionic surfactant is present in an amount of 1% to 40%.

11. A composition as claimed in any one of claims 1 to 10 wherein the surface active agent comprises a non-ionic surfactant.
12. A composition as claimed in claim 11 wherein the non-ionic surfactant is a water-soluble alcohol ethoxylate of HLB lower than 13.
13. A composition as claimed in claim 11 or 12 wherein the non-ionic surfactant is present in an amount of 1% to 15% by weight.
14. A composition as claimed in any one of claims 1 to 13 containing a cellulase.
15. A composition as claimed in claim 11 wherein the cellulase is present in an amount of 0.05% to 4% by weight of the composition.
16. A composition as claimed in any one of claims 1 to 15 including a builder.
17. A composition as claimed in claim 16 wherein the builder is present in an amount of 15% to 50% by weight.
18. A composition as claimed in claim 16 or 17 wherein the builder is sodium tripolyphosphate.
19. A composition as claimed in any one of claims 1 to 18 containing an alkaline material.
20. A composition as claimed in claim 19 wherein the alkaline material is sodium carbonate.
21. A composition as claimed in any one of claims 1 to 20 in powdered or granular form.

## INTERNATIONAL SEARCH REPORT

Intern. Application No

CT/GB 94/01882

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/00 C11D3/37 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FR,A,2 263 298 (BASF AG) 3 October 1975 see claim 1 ---	1
Y	TENSIDE SURFACTANTS DETERGENTS, vol.28, no.6, 1 November 1991, MÜNCHEN pages 428 - 433 H.-U. JÄGER; W. DENZINGER 'Wirkungsweise von Polymeren mit farbübertragungsinhibierenden Eigenschaften' see page 430; table 1 ---	1
A	DE,A,31 04 371 (HENKEL KGAA) 11 November 1982 see page 6, line 9 - line 16 --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
- 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

- 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- '&' document member of the same patent family

Date of the actual completion of the international search

25 November 1994

Date of mailing of the international search report

13.12.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Ketterer, M

## INTERNATIONAL SEARCH REPORT

Internat. Application No.

PCT/GB 94/01882

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 18598 (THE PROCTER & GAMBLE COMPANY) 29 October 1992 cited in the application see claims -----	1-21

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/GB 94/01882

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2263298	03-10-75	DE-A- 2410824	18-09-75
		AT-B- 356624	12-05-80
		BE-A- 826395	08-09-75
		CH-A- 586750	15-04-77
		GB-A- 1493085	23-11-77
-----			
DE-A-3104371	11-11-82	NONE	
-----			
WO-A-9218598	29-10-92	AU-A- 1757992	17-11-92
		AU-A- 1798692	17-11-92
		BR-A- 9205889	05-07-94
		CA-A- 2108164	13-10-92
		CA-A- 2108165	13-10-92
		CN-A- 1066878	09-12-92
		CN-A- 1067917	13-01-93
		EP-A- 0508034	14-10-92
		EP-A- 0508358	14-10-92
		JP-T- 6506497	21-07-94
		JP-T- 6506721	28-07-94
		NO-A- 933603	10-12-93
		NO-A- 933644	02-12-93
		WO-A- 9218597	29-10-92
-----			

**THIS PAGE BLANK (USPTO)**